Ecole Doctorale des Sciences Fondamentales

Title of the thesis: New fluorinated compounds for energy and environment: applications for the photogeneration of dihydrogen and photodecontamination of water

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Summary :

<u>Context:</u> Environment and Energy

Hydrogen is considered one of the more demanded synthetic energy carrier. However, since the production, packaging, storage, transfer and delivery of hydrogen gas are extremely energy consuming, hydrogen technology is currently more expensive than conventional energy sources and therefore alternatives to its production appear to be of great interest. In recent years photocatalytic water splitting using solar energy has been studied as a potential method for sustainable hydrogen production. It is reported in the literature that photocatalytic water splitting can be achieved using a photoelectrochemical cell containing a TiO_2 semi-conductor anode, a large number of semiconductors have been developed for this purpose. Unfortunately, most of them are wide band gap semiconductors and only active under UV light irradiation [1-5]. In addition to this ability to produce hydrogen, these materials are known for an efficient generation of oxygen reactive species, such as hydroxyl radicals, upon UV and/or visible radiations. Thus, they may also be used for decontamination of waters by oxidation of organic pollutants up to the mineralization. Moreover, several studies have clearly shown that the insertion of fluorine atoms in certain TiO_2 and ZnO structures clearly improves the efficiency in term of hydrogen production and photocatalytic activity [6-9]. The F doping reduces the recombination of free electron-hole pairs and then enhanced the photocatalytic activity, but F doping shifts the Fermi level position and increases the charge carrier concentration.

Within the present PhD thesis, we propose to design new materials by insertion of fluorine atoms into nanostructured materials of type: TiO_2/V_2O_5, TiO_2/MoO_3, … heterojunctions which are known for their good photocatalytic activities and H_2 generation, or by making heterojunctions between TiO_2 or ZnO with fluorinated compounds (BiOF, $Bi_2TiO_4F_2$, Zn(OH)F, …). These materials will be tested for their ability in terms of pollutants

photodegradation (hydroxyl radical formation) but also hydrogen generation. Thus the PhD will be implied:

- in the synthesis of these new materials and their characterisation and also their optimization.
- in the immobilization of the photocatalysts on appropriate supports and in testing them for their efficiency.
- the use of the photocatalysts for the photogeneration of hydrogen upon, first excitation in the UV region and second to their extension to the visible light.
- In the use of the photocatalysts for the oxidation of organic pollutants in aqueous media. This study will be performed from the kinetic as well as analytical point of view. The mechanism of organic oxidation will be deeply studied and the reactive oxygen species will be elucidated. The latter process will be explored using appropriate and selective probes and methods.

The supervisors in the teams MI and Photochemistry are experts in the synthesis and characterisation of the photocatalysts and also in the study of their photochemical behaviour and efficiency. The applicant must arise from a Master's degree or from an Engineering school in physical chemistry, chemistry or materials sciences.

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